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THE PHOTOCHEMISTRY OF ANTI-TRICYCLO[5.2.0.$0^{2,5}$]NONA-3,8-DIEN-9-ONE. FORMATION OF TETRACYCLO[6.1.0.$0^{2,9}$.$0^{4,7}$]NON-5-EN-3-ONE.

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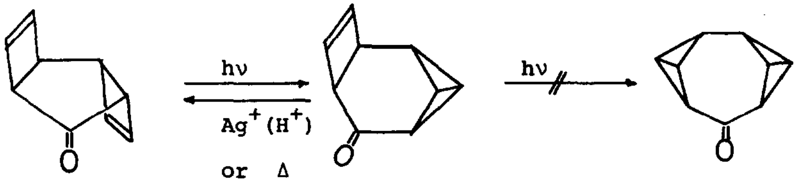
Recently, Cargill and coworkers[1] have reported that irradiation of anti-tricyclo[5.2.0.$0^{2,5}$]nona-3,8-dien-9-one(I)[1,2] in methylenechloride with "black-lights" gives homocubane as a major product. However, it may be expected that the photoisomerization of I which is a β·γ-unsaturated ketone produces the corresponding bicyclo[1.1.0]butane derivatives(II and III) via a triplet-excited state[3].

In this communication, I report the conversion of I into tetracyclo[6.1.0.$0^{2,9}$.$0^{4,7}$]non-5-en-3-one(II) which is a considerably interesting compound since it is not only a precursor of $(CH)_9$-X group[2,4] but also a bicyclo[1.1.0]-butane derivative[5].

Irradiation of a 0.6% solution of I in dry acetone with a 6-W Hg lamp gave II as a colorless oil in 16% yield(b.p. 43-44°/0.2mm). Identification of II is based on its spectral data, acid-catalyzed isomerization and thermal isomerization. The nmr spectrum of II shows two vinyl hydrogens at δ 6.22(s, br, 1H) and 5.95(m, 1H), and bicyclobutane hydrogens at δ 2.75(m, 1H), 2.57(m, 1H), 2.25(t, 1H, J=3.0 Hz) and 2.35(t, 1H, J=3.0 Hz). Its ir spectrum shows ν_{max}(film) 1695 cm^{-1} which indicates a 6-membered ring ketone. Its uv spectrum exhibits $n \rightarrow \pi^*$ transition at λ_{max} 299 nm(ε 126).

Since it has been known that a number of bicyclo[1.1.0]butanes undergo silver(I) ion catalyzed or acid catalyzed rearrangement[6], the ketone(II) in ether was treated with a 30% aqueous solution of silver tetrafluoroborate at room temperature to yield exclusively I. Further, II was injected into a gas chromatograph at 140° to produce the same ketone(I). The similar isomerizations were observed in the study of tricyclo[4.1.0.0^{2,7}]heptan-3-one[3].

It is interesting to note that no further rearranged product(**III**) was obtained in the above reaction. There are several features to rationalize the observation. It would appear that one of them must be instability of **III** as a result of the high strain energy of the molecule[7] under the reaction conditions. Investigations of the chemistry of **II** are continuing.



I **II** **III**

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7. The estimated strain energy for the parent hydrocarbon of **III** is 134.1 kcal/mol. The value is obtained by the sum of the strain of the component cycloheptane(6.3 kcal/mol.*) and two of bicyclobutane(63.9 kcal/mol.**).

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